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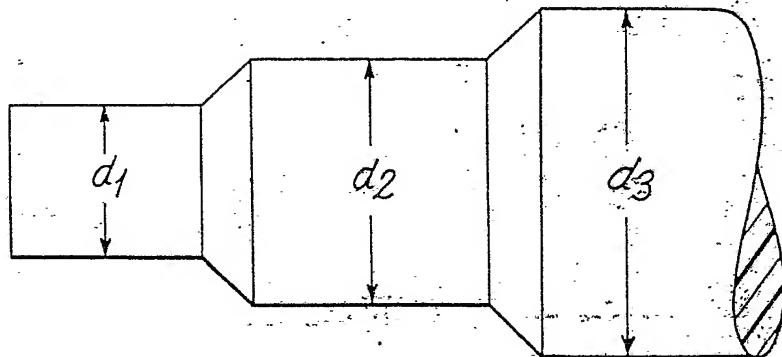
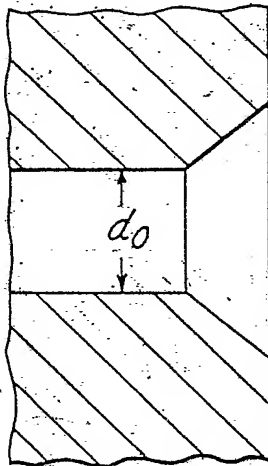
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(54) Title: POLYMER PROCESSING



$$R_{Ni} = \left( \frac{d_i}{d_0} \right)^2$$

(57) Abstract

Oriented thermoplastics having enhanced properties such as Young's modulus, resistance to creep, resistance to gas transport are prepared by drawing the thermoplastic in the solid phase through a die so that its plastic strain is progressively increased during start-up.

1. The purpose of this document is to provide information on the codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

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POLYMER PROCESSING

This invention relates to the deformation of thermoplastic polymers; more particularly, this invention relates to the solid phase deformation and concomitant orientation of orientable, thermoplastic polymers.

05 U.K. Patent No. 1311885 discloses a process for reducing the cross-sectional area of an article of an orientable, thermoplastic polymeric material by drawing the article, at a temperature below its melting point, through a well-lubricated die of smaller cross-sectional area than that of the article, which process  
10 comprises forming an integral, preferentially oriented nose at one end of the article by a solid phase deformation process, such that the tensile strength of the nose exceeds the draw tension to be applied to the article, gripping the nose and drawing the article through the die so as to induce a substantial degree of  
15 molecular orientation throughout the drawn article.

This patent specification further discloses that the process is preferably performed by utilising the technique of hydrostatic extrusion; indeed, every example of the invention does use this technique. However, and as the specification rightly points out,  
20 at the date of that specification simple hydrostatic extrusion was limited by a deformation ratio "boundary" above which further increase in the ratio of the cross-sectional area of the polymer billet to that of the extruder die orifice had no useful effect; relaxation effects resulted in an extrudate exhibiting die swell  
25 limiting the actual deformation ratio and orientation. These "boundaries" are given as low as 2.1:1 for polyvinyl chloride to 5.8:1 for glass fibre-filled polypropylene. The specification discloses overcoming this disadvantage by applying to the issuing extrudate a deforming draw tension, the complete process often  
30 being referred to as draw assisted extrusion.

U.K. Patent No. 1480479 discloses a process for the production of an oriented polymer material which comprises preparing a polymeric workpiece by cooling a semi-crystalline polymer having



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a natural draw ratio greater than 6 from the melt at a rate from 0.1 to 10°C per minute thereby obtaining the workpiece with substantially uniform morphology in cross-section; and deforming the workpiece below the melting point of the polymer by application  
05 of pressure.

This patent specification further discloses that by starting with a polymer of selected weight and number average molecular weights and thermal history it is possible to increase the deformation ratio "boundaries" to much higher levels. Moreover,  
10 at deformation ratios greater than about 8:1, and contrary to the teaching of U.K. 1311885, it is disclosed that die swell with lowered actual deformation is not encountered and thus, as is shown in Examples 2 and 3, the application to the issuing extrudate of a deforming draw tension is unnecessary.

15 According to the present invention, there is provided a process for the solid phase deformation of a workpiece of an orientable thermoplastic polymer, which process comprises: providing the workpiece of the essentially unoriented polymer at the entry side of a die; applying to the workpiece from the exit  
20 side of a die a draw tension insufficient to cause tensile failure of the workpiece; and drawing the workpiece through the die so that its plastic strain is progressively increased during start-up of the process.

The term "workpiece" as used herein includes bars, strips,  
25 rods, multifilaments, tubes and other cross-sections of solid or hollow stock. The term includes both billets and other forms of stock of greater length; indeed, continuous stock, which may be formed as the process is performed, may be utilised: examples include a polymer sheathed continuous core such as a metal wire,  
30 or continuous polymer rod, film or filaments.

The orientable thermoplastic polymer is desirably a semi-crystalline polymer, especially one which exhibits sufficient strain hardening and strain rate dependence of the flow stress to stabilise

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the neck formed under the desired drawing conditions. Preferred such polymers are unsubstituted or fluoro-substituted vinyl polymers and polyacetals, suitably a linear homo- or copolymer of ethylene or propylene with at least one comonomer, a vinylidene fluoride polymer or a homo- or co-polyoxymethylene.

Where it is intended to utilise the die drawing process of this invention to produce a product with enhanced Young's modulus; resistance to creep; resistance to gas transport; enhanced deadfold; or enhanced axial thermal conductivity then a workpiece of a linear homo- or copolymer of ethylene should desirably comprise a polymer having a weight average molecular weight ( $\bar{M}_w$ ) less than 1,000,000, suitably from 50,000 to 500,000, preferably from 70,000 to 400,000; one of a linear homo- or copolymer of propylene should desirably comprise a polymer having a  $\bar{M}_w$  from 150,000 to 800,000, preferably from 250,000 to 500,000.

However, the die drawing process of this invention may also be performed, to provide a more advantageous forming process but not the enhanced properties listed above, on a workpiece of an essentially unoriented but orientable, amorphous polymer or an essentially unoriented but orientable, semi-crystalline ultra high molecular weight polymer (for example, a linear homopolymer of ethylene having a  $\bar{M}_w$  about 3,000,000). It may likewise be utilised, but to a lower deformation ratio, in respect of those polymers which would otherwise give the enhanced properties listed above.

The thermoplastic polymer workpieces used in the process of this invention may be filled. Examples of useful fibrous fillers include glass, asbestos, metal, carbon and ceramic whiskers, such as those formed from silicon carbide. Examples of useful laminar fillers include mica, talc and graphite flakes. Chalk and fly ash may also be included. The amount of filler which may advantageously be included depends on the nature of the filler,

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but up to 50% by weight, preferably less than 30%, especially less than 20%, may be incorporated.

The term "essentially unoriented" as used herein means that the workpiece has incurred no orientation other than that minor  
05 amount which might be induced during formation of the workpiece, for example during billet moulding or melt extrusion, or during any subsequent shaping thereof, for example by machining, prior to the performance of the die drawing process of this invention.

Where it is not possible to use the polymer as received as a  
10 workpiece, the workpiece may be formed either in the batch or continuously. In either case, where the cross-sectional area of the workpiece is substantially greater than that, for example, of a textile filament care must be taken to ensure that the workpiece cools sufficiently slowly to prevent voids and stress cracking  
15 from occurring. At low cross-sectional area, surface cooling effects outweigh bulk conduction effects and the formation of voids and cracks is not found to pose any problem. Indeed, it is envisaged that the process of the invention applied to a workpiece, particularly a continuous workpiece, of low cross-sectional area,  
20 such as a filament or a film, will provide a practicable alternative to melt spinning or melt extrusion techniques for producing such material with enhanced Young's modulus.

In the case of a workpiece formed in the batch, for example a polymer billet, the following general methods have been found  
25 to be suitable. The polymer may be melted in a screw extruder; extruded or injected into a billet mould at a temperature about 30°C above its melting point and cooled under elevated pressure for 5 hours, or it may be melted in an extruder; extruded or injected into a cold billet mould; transferred to an oven for  
30 4 hours under ambient pressure at a temperature below its melting point but above its crystallisation temperature; and thereafter allowed to cool in the oven after the heating has been switched off. The polymer may also be injection moulded into an air or water cooled billet mould. Progressive immersion in the cooling

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fluid is preferred, thereby ensuring that solidification of the polymer takes place from the bottom of the mould thereby preventing the formation of internal voids due to shrinkage. Where the work-piece is to be hollow it may be formed in the batch by including  
05 a mandrel of appropriate cross-section, usually coaxially, in the mould. Alternatively stock of circular solid or hollow cross-section may be produced continuously using one of several processes known to those skilled in the art.

In accordance with the die drawing process of this invention  
10 the plastic strain of the workpiece is progressively increased during start-up of the process. This can be effected, in accordance with one embodiment of the invention, by utilising a workpiece wherein that end (herein termed the "nose") of the workpiece to which the draw tension is applied is of progressively reduced:  
15 (either continuously or in stages) cross section. (Hereinafter particular reference is made for convenience to stock of circular solid or hollow cross-section. The die drawing process of this invention is not, however, limited to such cross-sections) The first alternative may be effected either by fabricating the work-  
20 piece with a conical nose, for example, by machining the workpiece to form a conical nose, or moulding the billet with a conical nose. The semi-angle of the nose should be less than that of the die through which the workpiece is to be drawn. The second alternative may be effected by fabricating, for example by  
25 machining the workpiece so that it has at least one, and preferably a plurality, for example from 2 to 4, of stages of progressively reduced cross-section, which together form a nose as shown in Figure 3 of the accompanying drawing.

In accordance with another embodiment of the invention the  
30 plastic strain of the workpiece can be progressively increased by providing at the entry side of the die a workpiece of essentially uniform cross section and, during start-up of the process, progressively reducing the aperture of the die orifice.



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Both such embodiments may be effected simultaneously.

In both such embodiments, the nose is advanced to protrude through the die lips and is secured to tensioning means applied from the exit side of the die. A suitable arrangement includes  
05 a hauloff comprising a pair of serrated jaws in which the nose is gripped; a high tensile cable one end of which cable is attached to the jaws, the other to a winch or a loading station to which a turning moment or mass may be applied thereby applying a draw tension to the nose. The hauloff may also comprise, instead of  
10 a cable, any tension transmitting means used in the metal drawing art including a chain, a rack and pinion mechanism, a screw mechanism and a hydraulically operated draw mechanism. The hauloff may further comprise a pair of continuous contra-rotating friction belts, generally known as a "caterpillar".

15 The draw tension should be sufficient to draw the workpiece through the die but insufficient to cause tensile failure of the article; that is, the draw tension should be such that the true stress at any point of the product does not exceed its fracture stress at that point. A suitable maximum value of draw tension  
20 may readily be determined by routine experiment. In the case of strain hardening polymers, as the drawing progresses the flow stress of the strained portions of the workpiece increases. This will permit a greater draw tension to be applied (giving an increased plastic strain). This enables greater cross-sections  
25 of workpiece, or smaller apertures of die, or both, to be utilised also giving a further increase in plastic strain. These increases further strengthen the strained polymer so that the strain can be progressively increased during start-up until a product having desired final properties (for example, Young's modulus or cross-  
30 sectional area) is attained whereafter steady state processing conditions obtain.



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After a grippable length of the workpiece has been drawn through the die the unoriented part of its nose may be removed and the oriented grippable length re-gripped thereby enabling a higher load to be applied.

05 For a particular polymer, a steady state process is obtained for a given set of temperature, draw speed and deformation ratio. "Deformation ratio" as used herein is the ratio of the initial cross-sectional area of the workpiece to the final cross-sectional area of the product. These parameters vary implicitly, but it  
10 has been found possible, for a particular polymer, to set the die temperature (which will be only a nominal temperature for the polymer since the process is not an isothermal one) and the work-piece shape and vary, by experiment, the draw speed to obtain the desired deformation ratio.

15 For linear homo- and copolymers of ethylene the die temperature is desirably set within  $60^{\circ}\text{C}$  below the melting point of the polymer. More particularly, for such polymers of  $\bar{M}_w$  from 50,000 to 150,000, the die temperature is preferably from  $70^{\circ}\text{C}$  to  $100^{\circ}\text{C}$ ; and for such polymers of  $\bar{M}_w$  above 300,000 from  $70^{\circ}\text{C}$  to  $120^{\circ}\text{C}$ ;  
20 For linear homo- and copolymers of polypropylene of weight average molecular weight from 150,000 to 800,000 the die temperature may be set from  $20^{\circ} - 170^{\circ}\text{C}$ , preferably  $90^{\circ} - 130^{\circ}\text{C}$ . A die temperature of  $80^{\circ} - 170^{\circ}\text{C}$ , preferably  $150^{\circ} - 170^{\circ}\text{C}$  is suitable for homo- or copolyoxymethylene and of  $80^{\circ}\text{C}$  to  $165^{\circ}\text{C}$  is suitable for vinylidene  
25 fluoride polymers. The polymer temperature may be further controlled by utilising a die with a temperature controlled chamber which extends downstream.

It is feasible to use draw speeds greater than  $1\text{ cm min}^{-1}$  in the die drawing process of this invention; indeed, speeds of  
30  $50\text{ cm min}^{-1}$  or more are preferred.

Where hollow stock is being die drawn by the process of this invention it is essential to provide an appropriately dimensioned mandrel on the entry side of the die and protruding between the

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die lips to prevent collapse. In a continuous process this mandrel can suitably be of the "floating plug" type. In a batch process a fixed mandrel may be used.

A batch process may be converted to a continuous one by  
05 putting the upstream end of the deforming workpiece and the downstream end of stock of the same cross-section both in contact with a hot, stainless steel plate; removing the plate and welding the two polymer surfaces. Preferably such a weld should be at an angle of  $45^{\circ}$  or less to the axis of the stock.

10 Utilising the die drawing process of this invention on polymers which show adequate strain hardening and strain rate dependence of the flow stress, it is possible to obtain deformation ratios of at least 10, preferably 20 or even more.

The invention will now be more particularly described, by  
15 way of example, with reference to the accompanying drawings in which:

Figure 1 represents an axial section of a coextrusion line in accordance with the invention; and

Figure 2 represents an axial section of an automated continuous extrusion line in accordance with the invention.

20 In Figure 1, a polymer coating 1 is supplied as melt flow from an extruder fitted with a crosshead annular die 2 through the centre of which the member to be coated 3 (such as cable, wire, rod or tube) is allowed to pass. The melt then passes through a cooling zone 4 where it is solidified. At the end of this zone  
25 the solidified coating 1 is essentially isotropic and is not in intimate contact with the surface of the member to be coated 3. Both member and isotropic coating then pass into a drawing block 5 of similar design to that already described and are heated to the drawing temperature. The polymer coating is next drawn through the  
30 converging die 6 mounted in the drawing block. Deformation of the polymer continues beyond the drawing block for some distance before it becomes "frozen-out". At this stage both member and coating are travelling with the same velocity, and the coating is

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in intimate contact with the member. The velocity of the process is controlled and determined by a haul-off "caterpillar" device 7 situated downstream from the final deformation zone.

The ratio of the cross-sectional area of the isotropic  
05 polymer tube entering the die block to that of the annular clearance between coated member and die bore is of great importance, as will be understood from the foregoing description of the process. This ratio is controlled and determined by the rate of output of the melt extruder which supplies the crosshead die. This  
10 embodiment of the invention can be used to coat several items simultaneously; used where the cross-section is not circular; or used where two or more different polymers are co-extruded.

In Figure 2 a polymer billet 8 is continuously extruded through a die 9 as described in British patent application 15023/79.  
15 The billet is then advanced to a drawing block 10 and drawn by a haul-off device (not shown) through a converging die 11 mounted in the drawing block. The haul-off velocity and the temperatures of the billet 8 and the drawn product 12 are continuously monitored; their values being input into a computer 13 whence output  
20 regulating the melt extrusion rate and quality given by the extruder 14 is provided to the hopper feed 15, the screw drive 16, the barrel heater 17 and the infinitely variable orifice controlled by butterfly valve 18.

In accordance with a further aspect of this invention, there  
25 are provided homo- and copolymers of polypropylene which have been deformed by passage through a die in the solid phase having a Young's modulus greater than 18, suitably greater than 20, preferably greater than 23 GPa, especially greater than 25 GPa. This invention further provides a homo or copolyoxymethylene  
30 which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 25 GPa, preferably greater than 27 GPa. This invention further provides



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a vinylidene fluoride polymer which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 3 GPa, suitably greater than 5 GPa preferably greater than 8 GPa. This invention also provides copolymers of linear polyethylene, particularly copolymers comprising a minor amount of hexene-1, especially those which have been deformed by passage through a die in the solid phase, having a Young's modulus greater than 30 GPa, preferably greater than 40 GPa. Such copolymer materials cannot be produced at high deformation ratios by conventional drawing or solid state extrusion. This invention further provides a Portland cement or concrete mass incorporating fibres either prepared as such or by fibrillating a film prepared by the process of this invention, particularly fibres of an ethylene-hexene-1 copolymer.

The advantages of the die drawing process of this invention over hydrostatic extrusion will be manifest to those skilled in the art. Thus, it obviates the necessity of a batch process and dispenses with expensive and potentially hazardous pressure equipment. It is also found that, and in contrast to hydrostatic extrusion, throughput increases with increasing deformation ratio.

The following Examples illustrate the invention.

Modulus values were determined from a flexural (three-point bend) test at 20°C. This was accomplished by applying a dead load to the test specimen and measuring the deflection after 10 seconds. The ratio of span to specimen thickness was maintained at 80 or higher. The maximum strain at any point in the specimen was less than 0.001.

#### EXAMPLE 1

A polypropylene block copolymer having weight average molecular weight of 650,000 (PROPATHENE GSE 108 ex I.C.I.) was melted at 250°C in an extruder; extruded into a billet mould at 160°C; and cooled under elevated pressure for 5 hours. The initial, isotropic



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billet was then machined so that the dimensions shown in the Figure in the accompanying drawing are:

$$d_1 = 7\text{mm}, d_2 = 10.4\text{mm}, d_3 = 15.8\text{mm}$$

The machined billet was then advanced into a conical die of 15° semi-angle and at a temperature set at 110°C. The die had a bore diameter of 7mm so that the nominal deformation ratios shown in Figure 3 of the accompanying drawings are:

$$R_{N1} = 1, R_{N2} = 2.2, R_{N3} = 5.1$$

The protruding nose of the billet formed by the first stage was gripped at the exit side of the die and the billet, at an initial temperature of 110°C, was drawn through the die at a speed of 10mm min<sup>-1</sup> at a tension of 32.5 kg wt until all of the second stage had been drawn. The grip was then repositioned on part of the billet corresponding to the second stage and drawing recommenced, until sufficient of the third stage had been drawn through the die to enable the grip to be affixed thereto, at a draw speed of 10 mm min<sup>-1</sup> at a tension of 92.5 kg wt. Thereafter the grip was finally positioned on the drawn part of the third stage and the remainder thereof was drawn through the die at a draw speed of 500mm min<sup>-1</sup> at a tension of 152 kg wt to give an oriented rod of actual deformation ratio 12.7 (average diameter 4.45mm) and a flexural Young's modulus of 15.1 GPa (+ 1.4 GPa).

In similar experiments a modulus of 20.6 GPa (+ 2.0 GPa) was achieved.

## 25 EXAMPLE 2

Example 1 was repeated using a high density polyethylene homopolymer of  $\bar{M}_w$  312,000,  $\bar{M}_w$  33,000 (HO20-54P ex BP Chemicals). The machined billet had  $d_1 = 5\text{mm}$ ,  $d_2 = 8.9\text{mm}$  and  $d_3 = 12.0\text{mm}$  and was drawn through a conical die of 15° semi-angle with its temperature set at 100°C. The die had a bore of 5.3mm so that  $R_{N1} = 1$ ,  $R_{N2} = 2.8$  and  $R_{N3} = 5.2$ . The respective draw speeds and tensions were 10mm min<sup>-1</sup> at 22 kg wt; 10mm min<sup>-1</sup> at 55 kg wt and 500mm min<sup>-1</sup> at 78 kg wt.



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The oriented rod had an actual deformation ratio of 10 (average diameter 3.88mm) and a flexural Young's modulus of 14 GPa.

EXAMPLE 3

Example 1 was repeated using polyoxymethylene of  $\bar{M}_n$  45,000 and  $\bar{M}_w/\bar{M}_n$  slightly greater than 2 (Delrin 500 ex Du Pont). The die had its temperature set at 160°C.

The oriented rod had an actual deformation ratio of 12.6 and a flexural Young's modulus of 20 GPa.

EXAMPLE 4

10 A high density polyethylene homopolymer of  $\bar{M}_w$  135,000,  $\bar{M}_n$  25,500 and melt flow index of 0.6 dg min<sup>-1</sup>. (006-60 ex BP Chemicals) was injection moulded using a mould with a 10mm diameter cylindrical cavity. The barrel temperature was 190°C, and the mould temperature was 110°C. The mould was held under  
15 injection pressure for 10 minutes to allow cooling and solidification to take place.

The initial isotropic billet had a diameter of 7mm one end of which was machined to give an essentially conical nose of 5° semi-angle which was extended for 20mm as a rod of diameter 4mm  
20 for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

The protruding nose of the billet was gripped at the exit  
25 side of the die and the billet, at an initial temperature of 110°C, was drawn through the die at an initial speed of 5mm min<sup>-1</sup>. After 100mm of material had been drawn through the die, the drawing was stopped and the product was cut off 20mm from the die. The oriented material protruding from the exit side of the die  
30 was then regripped and drawing was recommenced at 5mm min<sup>-1</sup>. The load rose to 22 kg and remained constant thereafter. The draw speed was then increased progressively to 66mm min<sup>-1</sup>.

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An oriented rod of actual deformation ratio 23.5 and a flexural Young's modulus of 51 GPa was obtained.

EXAMPLE 5

A high density polyethylene homopolymer (HO20-54P ex BP  
05 Chemicals) was compression moulded as follows: a two-part mould was filled with polymer powder, heated to 210°C and left for 20 minutes to attain thermal equilibrium. The mould was then placed between the platens of a press and the powder compressed into a cavity of dimensions 20mm x 20mm x 200mm. A force of 1200 KN  
10 was used. The platens were then water cooled and moulding pressure maintained until the mould temperature had fallen below 80°C.

The initial isotropic billet had a diameter of 12mm one end of which was machined to give an essentially conical nose of 5°  
15 semi-angle which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of 15° semi-angle, a bore diameter of 4mm and a temperature set at 100°C.

20 The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of 100°C, was drawn through the die at an initial speed of 5mm min<sup>-1</sup>. After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20mm from the die.

25 The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 40 kg. The draw speed was then progressively increased to a steady state value of 77 kg.

An oriented rod of actual deformation ratio 11.2 and a  
30 flexural Young's modulus of 13 GPa was obtained.

EXAMPLE 6

A high density polyethylene homopolymer of  $\overline{M}_w$  about 3,500,000 (Hostalen GUR ex Hoechst) was used as received as isotropic rod



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stock of 8mm diameter. One end of this was machined to give an essentially conical nose of  $5^{\circ}$  semi-angle which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

05 The machined billet was then advanced into a conical die of  $15^{\circ}$  semi-angle, a bore diameter of 4mm and a temperature set at  $130^{\circ}$ .

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of  $130^{\circ}\text{C}$ , was drawn through the die at an initial speed of  $5\text{mm min}^{-1}$ .

10 After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 4 kg. The draw speed was then gradually increased to  $200\text{mm min}^{-1}$ . The  
15 load rose to a steady state value of 20 kg.

An oriented rod of actual deformation ratio 5 and a flexural Young's modulus of 1.76 GPa was obtained.

#### EXAMPLE 7

A copolymer of ethylene and hex-1-ene of  $\bar{M}_w$  155,000,  $\bar{M}_n$  16,900  
20 and 0.9 to 1.5 n-butyl branches per  $10^3$  carbon atoms (002-55 ex BP Chemicals) was extrusion moulded in the following manner:

A melt extruder was used to fill a cylindrical aluminium mould, which was then placed vertically in an oven to allow solidification of the polymer. A temperature gradient was main-  
25 tained in the oven so that the bottom of the mould was at  $110^{\circ}$  and the top at  $120^{\circ}\text{C}$ . This procedure ensured that solidification of the polymer took place from the bottom of the mould upwards, preventing the formation of internal voids due to shrinkage.

The initial, isotropic billet had a diameter of 9mm one end  
30 of which was machined to give an essentially conical nose of  $5^{\circ}$  semi-angle which was extended as a rod of diameter 4mm for gripping purposes.



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The machined billet was then advanced into a conical die of  $15^{\circ}$  semi-angle, a bore diameter of 4mm and a temperature set at  $100^{\circ}\text{C}$ .

05 The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of  $100^{\circ}\text{C}$ , was drawn through the die at an initial speed of  $5\text{mm min}^{-1}$ . After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20mm from the die. The oriented material protruding from the exit side of the die was  
10 then regripped and drawing was recommenced. The load rose to 31 kg. The draw speed was then gradually increased to a steady state value of  $25\text{mm min}^{-1}$ .

An oriented rod of actual deformation ratio 27 and a flexural Young's modulus of 62 GPa was obtained.

15 EXAMPLE 8

A high density polyethylene homopolymer (006-60 ex BP Chemicals) was injection moulded using a mould with a cylindrical cavity. The barrel temperature was  $190^{\circ}\text{C}$  and the mould temperature was  $110^{\circ}\text{C}$ . The mould was held under injection pressure for 10 minutes to allow solidification to take place.

20 The initial, isotropic tube billet was machined from the moulding. The tube billet had an internal diameter of 2mm and an external diameter of 8mm. An essentially conical nose of  $5^{\circ}$  semi-angle which was extended as a tube with an outer diameter of 4mm for gripping purposes was machined on one end of the billet  
25 surface.

The machined billet was then advanced into a conical die of  $15^{\circ}$  semi-angle, a bore diameter of 4mm and a temperature set at  $100^{\circ}\text{C}$ . A fixed mandrel of 2mm diameter was then inserted into the billet.

30 The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of  $100^{\circ}\text{C}$ , was drawn through the die at an initial speed of  $5\text{mm min}^{-1}$ .



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After 100mm of material had been drawn through the die the drawing was stopped and the product cut off 20mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing recommenced. The load rose to  
05 30 kg. The draw speed was then progressively increased to a steady value of  $50\text{mm min}^{-1}$ . The load increased to a steady state value of 31 kg.

An oriented tube of actual deformation ratio 13 and a flexural Young's modulus of 23 GPa was obtained.

10 EXAMPLE 9

A polypropylene copolymer (PROPATHENE GSE 108 ex I.C.I.) was extrusion moulded into a tube billet mould.

The procedure of Example 8 was then essentially repeated with the internal diameter of the tube billet 2mm, the external  
15 diameter 7.17mm. The initial temperature of the polymer was  $110^{\circ}\text{C}$  and the steady state draw speed was  $40\text{mm min}^{-1}$ .

An oriented tube of actual deformation ratio 6.5 and a flexural Young's modulus of 6.3 GPa was obtained.

EXAMPLE 10

20 Twenty-four filaments of a high density polyethylene homopolymer of  $\bar{M}_w$  102,000,  $\bar{M}_n$  6,200 (Rigidex 50 ex BP Chemicals) were melt spun into a glycerol bath at  $118^{\circ}\text{C}$ . The isotropic filaments had a diameter of 1.36mm. Each filament was necked by contact  
25 inserted into a conical die of  $15^{\circ}$  semi-angle, a bore diameter of 4mm and a temperature set at  $100^{\circ}\text{C}$ .

The protruding tow was then gripped at the exit side of the die and, at an initial temperature of  $100^{\circ}\text{C}$ , was drawn through the die at a draw speed which was progressively increased to a steady  
30 state value of  $100\text{mm min}^{-1}$ .

An oriented tow of filaments of polygonal cross-section and deformation ratios of from 15 to 20 was obtained. The flexural Young's modulus of individual filaments was from 32 to 40 GPa.

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EXAMPLE 11

A polymer composite containing 75% polypropylene ("Propathene" ex I.C.I.) and 25% chopped glass fibres (by weight) was moulded into rod using a melt extrusion process.

05 The initial billet machined from the moulded rod had a diameter of 9.8mm, one end of which was machined to give an essentially conical nose of  $5^\circ$  semi-angle which was extended as a rod of 4mm diameter for gripping purposes.

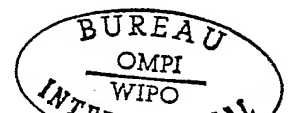
10 The machined billet was then advanced into a conical die of  $15^\circ$  semi-angle, a bore diameter of 4mm and a temperature set at  $110^\circ\text{C}$ .

The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of  $110^\circ\text{C}$ , was drawn through the die at an initial speed of  $5\text{mm min}^{-1}$ . After 15 100mm of material had been drawn through the die, the drawing was stopped and the product cut off 20mm from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 69 kg. The draw speed was then increased to a steady state value of 20  $50\text{mm min}^{-1}$ . An oriented composite rod of actual deformation ratio 11 and a flexural Young's modulus of 14 GPa was obtained.

EXAMPLE 12

A polyvinylidene fluoride homopolymer of  $\overline{M}_w 351,200$ ,  $\overline{M}_n 171,000$  (Solef XION, ex Solvay) was injection moulded using a 25 mould with a 10mm diameter cylindrical cavity. The barrel temperature was  $220^\circ\text{C}$  and the mould temperature was  $20^\circ\text{C}$ . The mould was held under injection pressure for 5 minutes, during which time it was cooled by progressive immersion in a water bath. This procedure ensured that solidification of the polymer took 30 place from the bottom of the mould upwards, preventing the formation of internal voids due to shrinkage.

The initial isotropic billet was machined to a diameter of 9.80mm, one end being further machined to give an essentially



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conical nose of  $5^{\circ}$  semi-angle, which was extended for 20mm as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of  $15^{\circ}$  semi-angle, a bore diameter of 4mm and at a temperature  $140^{\circ}\text{C}$ .

05 The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of  $140^{\circ}\text{C}$ , and was drawn through the die at a speed of  $10\text{mm min}^{-1}$ . After 100mm of material had been drawn through the die, the drawing was stopped and the product was cut off 20mm from the die. The oriented  
10 material protruding from the exit side of the die was then regripped, and drawing was recommenced at  $10\text{mm min}^{-1}$ . The load rose to a value of 112 kg and remained constant thereafter.

An oriented rod of actual deformation ratio 6.00 and a flexural Young's modulus of 3.96 GPa was obtained.

15 In the case of polyvinylidene fluoride molecular weight restrictions are not found to be particularly critical. Desirably, however, the polyvinylidene fluoride has a number average molecular weight from  $1.0$  to  $1.9 \times 10^5$ , preferably from  $1.3$  to  $1.8 \times 10^5$ , and a weight average molecular weight from  $2 \times 10^5$   
20 to  $8 \times 10^5$ .

Such material may be die-drawn to deformation ratios in excess of 6, for example 6.5 to 8 or even more.

#### EXAMPLE 13

A high density polyethylene homopolymer of  $\bar{M}_w$  67,800,  
25  $\bar{M}_n$  13,350 (140-60 ex BP Chemicals) was extrusion moulded into a cylindrical tube, which was then placed vertically in an oven to allow slow cooling solidification of the polymer.

An isotropic billet for die-drawing was machined to a diameter of 8.94 mm one end being a cone of  $5^{\circ}$  semi-angle which  
30 was extended as a rod of 4mm diameter for gripping purposes.

The machined billet was advanced into a conical die of  $15^{\circ}$  semi-angle and bore diameter of 4mm, set at a temperature of  $110^{\circ}\text{C}$ .

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The protruding nose of the billet was gripped at the exit side of the die and the billet, at an initial temperature of  $110^{\circ}\text{C}$ , was drawn through the die at a preliminary draw speed of  $5\text{mm min}^{-1}$ . After a length of material had been drawn through the die the process was stopped and the product was cut off at a short distance from the die. The oriented material protruding from the exit side of the die was then regripped and drawing continued. The haul-off speed was increased to  $30\text{mm min}^{-1}$  whereupon the load rose to a steady value of 15 kg.

An oriented rod of actual deformation ratio 23.4 and a flexural Young's modulus of 45.4 GPa was obtained.

#### EXAMPLE 14

A copolymer of ethylene and hex-1-ene (002-55 ex BP Chemicals) was extrusion moulded in the following manner:

A melt extruder was used to fill a cylindrical aluminium mould, which was then placed vertically in an oven at  $120^{\circ}\text{C}$  to allow solidification of the polymer.

The initial, isotropic billet had a diameter of 11.31mm and one end was machined to give a conical nose of  $5^{\circ}$  semi-angle which was extended as a rod of diameter 4mm for gripping purposes.

The machined billet was then advanced into a conical die of  $15^{\circ}$  semi-angle, a bore diameter of 4mm and a temperature set at  $100^{\circ}\text{C}$ .

The protruding nose of the billet was gripped at the exit side of the die and then the billet, at an initial temperature of  $100^{\circ}\text{C}$ , was drawn through the die at a preliminary draw speed of  $5\text{mm min}^{-1}$ . After a length of material had been drawn through the die the process was stopped and the product was cut off at a short distance from the die. The oriented material protruding from the exit side of the die was then regripped and drawing was recommenced. The load rose to 65 kg as the draw speed was gradually increased to a steady state value of  $100\text{mm min}^{-1}$ .

An oriented rod of actual deformation ratio 11.5 and a flexural Young's modulus of 15.2 GPa was obtained.



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CLAIMS

1. A process for the solid phase deformation of a workpiece of an orientable, thermoplastic polymer, which process comprises: providing the workpiece of the essentially unoriented polymer at the entry side of a die; applying to the workpiece from the exit side of a die a draw tension insufficient to cause tensile failure of the workpiece; and drawing the workpiece through the die so that its plastic strain is progressively increased during start-up of the process.
2. A process according to Claim 1 wherein the polymer is a semi-crystalline polymer.
3. A process according to Claim 2 wherein the polymer is an unsubstituted or fluoro-substituted vinyl polymer or a polyacetal.
4. A process according to Claim 3 wherein the polymer is a linear homo- or copolymer of ethylene or propylene with at least one comonomer.
5. A process according to Claim 4 wherein the polymer is a linear homo- or copolymer of ethylene of  $\overline{M}_w$  from 50,000 to 500,000.
6. A process according to Claim 5 where the die temperature is from 60°C below to below the melting point of the polymer.
7. A process according to Claim 4 wherein the polymer is a linear homo- or copolymer of propylene of  $\overline{M}_w$  from 150,000 to 800,000.
8. A process according to Claim 7 wherein the die temperature is from 20°C to 170°C.
9. A process according to Claim 3 wherein the polymer is a polyoxymethylene.
10. A process according to Claim 9 wherein the die temperature is from 80°C to 170°C.
11. A process according to Claim 3 wherein the polymer is a vinylidene fluoride polymer.
12. A process according to Claim 11 wherein the die temperature is from 80°C to 165°C.



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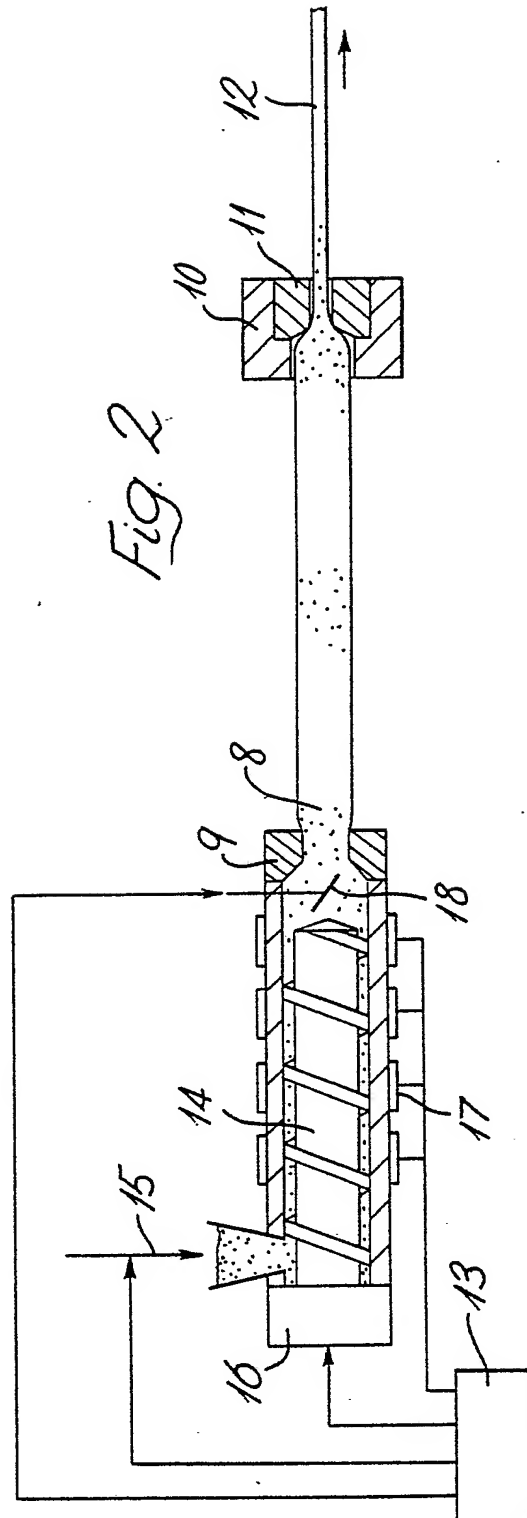
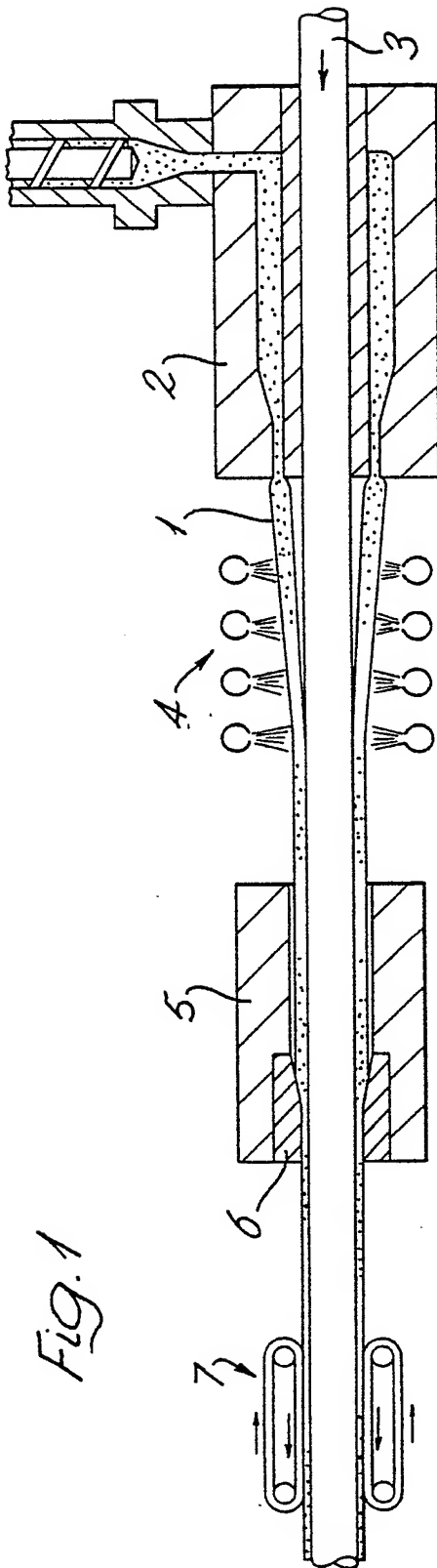
13. A process according to any preceding claim wherein the polymer is filled.
14. A process according to any preceding claim wherein that end of the workpiece to which the draw tension is applied is of progressively reduced cross section.
15. A process according to any preceding claim wherein the aperture of the die is progressively reduced during start-up of the process.
16. A process according to any preceding claim wherein the draw speed is at least  $50\text{cm min}^{-1}$ .
17. A process according to any preceding claim which is continuous.
18. A process according to Claim 17 wherein the upstream end of a discrete workpiece being deformed in accordance with Claim 1 is welded to the downstream end of continuous stock of the same polymer and cross-section.
19. A process according to Claim 17 or 18 wherein the workpiece is continuously formed in situ.
20. A process according to any preceding claim where the workpiece is a filament, film or tube.
21. A process according to any preceding claim wherein the deformation ratio is greater than 10.
22. An oriented thermoplastic polymer whenever prepared by the process of any preceding claim.
23. A homo- or copolymer of propylene which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 18 GPa.
24. A homo- or copolyoxymethylene which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 25 GPa.
25. A vinylidene fluoride polymer which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 3 GPa.

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26. A copolymer of ethylene which has been deformed by passage through a die in the solid phase and having a Young's modulus greater than 10 GPa.
27. A copolymer according to Claim 26 having a Young's modulus greater than 30 GPa.
- 05 28. A copolymer of ethylene which has a Young's modulus greater than 40 GPa.
29. A copolymer according to any of Claims 26 to 28 wherein the comonomer comprises up to 5% of hexene-1.
- 10 30. A Portland cement, concrete or thermoset mass into which fibres according to any of Claims 22, 23 and 26 to 29 have been introduced.

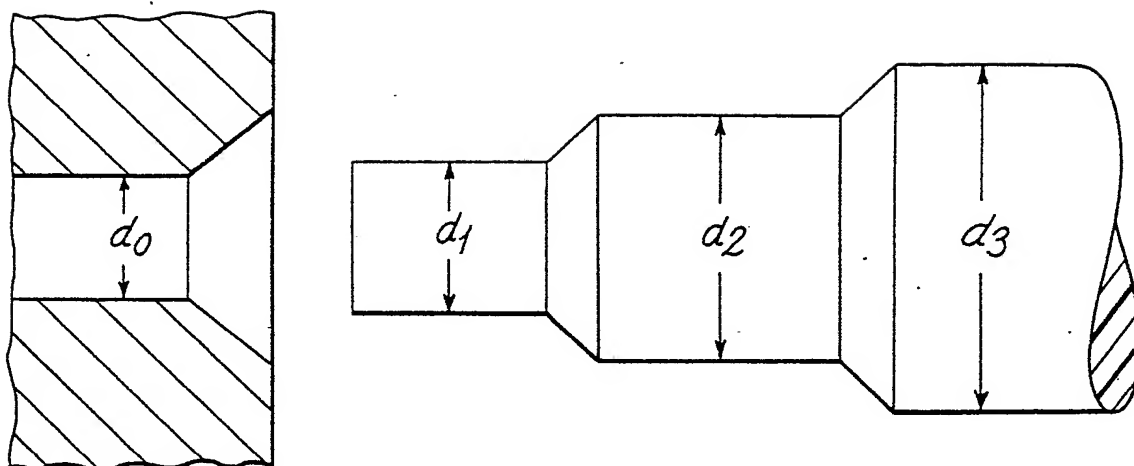


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Fig. 3



$$R_{Ni} = \left( \frac{d_i}{d_0} \right)^2$$

# INTERNATIONAL SEARCH REPORT

International Application No PCT/GB 80/00099

## I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) <sup>3</sup>

According to International Patent Classification (IPC) or to both National Classification and IPC

Int.Cl.<sup>3</sup> B 29 C 17/02

## II. FIELDS SEARCHED

### Minimum Documentation Searched <sup>4</sup>

Classification System

Classification Symbols

Int.Cl.<sup>3</sup> B 29 F; B 29 D; B 29 C

Documentation Searched other than Minimum Documentation  
to the Extent that such Documents are Included in the Fields Searched <sup>5</sup>

## III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>14</sup>

Category <sup>*</sup>	Citation of Document, <sup>15</sup> with indication, where appropriate, of the relevant passages <sup>17</sup>	Relevant to Claim No. <sup>15</sup>
	NL, A, 6612434, published December 27, 1966 see figures 1,2; page 3, lines 11 to 36, Du Pont --	1,3,9,10,14, 15,16,17,20, 21,22,23
	GB, A, 953734, published April 2, 1964 see the whole document, R.A. Covington --	1,4,5,6,14, 20
	US, A, 2291670, published August 4, 1942 see the whole document, R.M. Wiley --	1,15,16,17, 19,20
	US, A, 3275730, published September 27, 1966 see figures 1 to 4; column 3, line 73. to column 4, line 64, Hercules --	1,4,5,6,7,8, 11,12,15,16, 17,19,20
	US, A, 4021521, published May 3, 1977 see the whole document, B.A.S.F. -----	3,13,19,20

### \* Special categories of cited documents: <sup>16</sup>

"A" document defining the general state of the art

"E" earlier document but published on or after the international filing date

"L" document cited for special reason other than those referred to in the other categories

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but on or after the priority date claimed

"T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention

"X" document of particular relevance

## IV. CERTIFICATION

Date of the Actual Completion of the International Search <sup>1</sup>

15th August 1980

Date of Mailing of this International Search Report <sup>2</sup>

27th August 1980

International Searching Authority <sup>1</sup>

European Patent Office

Signature of Authorized Officer <sup>20</sup>

G.L.M. Kruidenberg